

PATENT SPECIFICATION

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(54) BRANCHED CHAIN ALIPHATIC ESTERS

5 (71) We, THE BRITISH PETROLEUM COMPANY LIMITED, of Britannic House, Moor Lane, London, E.C.2., England, a company incorporated in accordance with the Laws of England, do hereby declare the invention for which we pray that a patent may be granted to us, and the method by which it is to be performed to be particularly described in and by the following statement:—

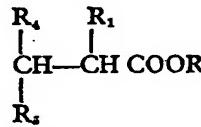
10 10 This invention relates to esters of carboxylic acids, and to methods of making them. More particularly it relates to esters of higher branched chain carboxylic acids.

15 By higher branched chain carboxylic acids are meant branched chain carboxylic acids containing a total of fourteen or more carbon atoms.

20 Straight chain carboxylic acids and their esters are, in general, well known compounds and are used in the preparation of soaps, greases and the like. The fatty acids and their esters are especially well characterised as they occur in nature.

25 It has now been found that esters of the higher branched chain carboxylic acids can be prepared by the reaction of a carboalkoxy carbene radical with a hydrocarbon containing at least twelve carbon atoms.

30 The invention consists in a method of preparing esters of higher branched chain carboxylic acids of general formula:



35 where R_4 and R_2 are saturated straight chain hydrocarbyl radicals which together contain at least eleven carbon atoms, and R_1 is hydrogen or an alkyl radical and R is a hydrocarbyl radical, such as alkyl, cycloalkyl, phenyl and substituted phenyl.

[Price 25p]

40 Which comprises reacting a saturated straight chain hydrocarbon having at least twelve carbon atoms with a carbohydrocarbyloxy carbene of general formula: CR_1COOR where R is a hydrocarbyl radical and R_1 is hydrogen or an alkyl radical.

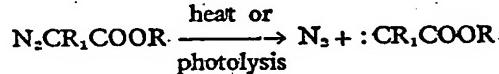
45 The preferred hydrocarbons used in the invention are the aliphatic hydrocarbons, preferably the straight chain paraffins containing from twelve to fifty carbon atoms, such as dodecane, tridecane, tetradecane, pentadecane and higher paraffins.

50 The preferred carbohydrocarbyloxy carbenes are those in which R is an alkyl group, preferably a C_{1-4} alkyl group and R_1 is hydrogen or a C_{1-4} alkyl group. The most preferred carboalkoxy carbene is that in which R_1 is hydrogen.

55 Carbenes are reactive diradicals and can be prepared by photolysis or thermal decomposition of compounds such as diazo compounds, ketenes and diazirines. Typical useful diazo compounds are diazoalkanes, alkyl diazoesters and diazoketones.

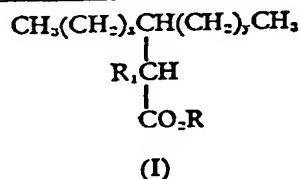
60 The preferred carboalkoxy carbenes used in the present invention can be prepared by the standard methods, and are preferably prepared by the photolytic or thermal decomposition of alkyl diazocarboxylates.

65 The decomposition of alkyl diazo carboxylates takes place according to the equation:—

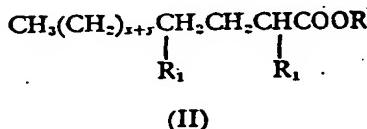


70 where R and R_1 are as defined above.

75 When the carboalkoxy carbenes are reacted with a straight chain aliphatic hydrocarbon of general formula $CH_3(CH_2)_nCH_3$, where n is 10 or greater, the product consists predominantly of branched chain esters of formula I, with a minor proportion of straight chain esters of formula II;



and



where R and R₁ are as defined above x and y are integers, one of which may be zero and x + y + 1 = n.

The precise mechanism of this reaction is not, at present, known certainly but carbenes solution is added to the bulk of the hydrocarbons by insertion into a C—H bond.

The reaction of the hydrocarbon with the carboalkoxycarbene is preferably carried out by forming the carbene radical in the presence of the hydrocarbon.

When a carboalkoxycarbene is formed by the photolytic decomposition of an alkyl diazocarboxylate, the alkyl diazocarboxylate can either be added dropwise to the hydrocarbon whilst the hydrocarbon is being irradiated, or more preferably, the alkyl diazocarboxylate is dissolved in part of the hydrocarbon, and this solution is added to the bulk of the hydrocarbon whilst the bulk of the hydrocarbon is being irradiated.

Radiation having a wave-length of between 2,500 Å and 5,000 Å, and preferably between 3,000 Å and 5,000 Å, can be used for the decomposition of alkyl diazocarboxylates. The exact wave-lengths used will depend on the nature of the alkyl diazocarboxylate and the hydrocarbon. A suitable source of radiation is a mercury arc reactor.

Preferably the carbene precursor is added to the hydrocarbon before formation of the carbene, so that when the carbene is formed it is surrounded by an environment of hydrocarbon molecules. High dilution of the carbene precursor is preferred.

When the carboalkoxycarbene is formed by the thermal decomposition of an alkyl diazocarboxylate, similar techniques to those utilised in the photolytic decomposition of alkyl diazocarboxylates can be used. The alkyl diazocarboxylates can either be added dropwise to the heated hydrocarbon, or, more preferably the alkyl diazocarboxylate is dissolved in part of the hydrocarbon, and this solution is added to the bulk of the hydrocarbon.

The thermal decomposition of the alkyl diazocarboxylate is preferably carried out at a temperature above 150°C.

Carbenes are generally considered to attack C—H bonds in aliphatic hydrocarbons in a

non-discriminatory manner, particularly in the liquid phase. In gas phase reactions, preference for attack at the primary C—H bonds relative to secondary C—H bonds has been noted. In our liquid-phase studies we have found, unexpectedly, that there is some preference for attack on the C₂ carbon atom of aliphatic hydrocarbons, i.e., in the formula (I) above when x = 0. Furthermore, the closer the methylene group is to the centre of the hydrocarbon molecule, the smaller is the amount of attack on that methylene group, i.e., there is a gradual decrease in the amount of products formed by attack at individual methylene groups in going from C₂ to C₆ in n-hexadecane.

The aliphatic hydrocarbons useful in the invention can be prepared from petroleum fractions by distillation followed by selective absorption or solvent extraction.

The esters of the present invention can readily be transesterified by conventional means to form other esters of branched chain aliphatic acids, and thus a wide variety of esters can be produced. The esters can also be hydrolysed or saponified to produce the parent branched chain aliphatic acids and salts thereof. These compounds can also be used as intermediates in the preparation of a range of compounds which contain the branched chain structure which is present in the esters of the present invention.

As is well known long chain esters have many uses for example; as plasticizers, lubricants and in the formation of oil soluble substances for detergents and emulsifiers.

Preparation of branched chain aliphatic esters by the method of the invention is described in the following Examples.

In these Examples, the important effect of dilution of the carbene precursor in the hydrocarbon is illustrated. To obtain satisfactory yields it is preferred to have the carbene surrounded by hydrocarbon molecules when it is formed, in order to cut down by-product formation from carbene/carbene and carbene/carbene precursor interactions. Therefore a molar ratio of hydrocarbon to carbene precursor of at least 2:1 and preferably as high as 100:1 should be employed.

EXAMPLE 1

Reaction with n-Hexadecane

Ethyl diazoacetate (2.55 g. 0.0228 mole) was added in 10 equal aliquots, over a period of five hours to n-hexadecane (24.0 g. 0.106 mole) i.e. in a molar ratio of 4/1 hydrocarbon/carbene precursor, maintained at 20°C and irradiated in a medium pressure mercury arc reactor. The photolysis was continued for a further sixteen hours. During the addition, removal of wall deposits from the inner surface of the reactor, in contact with the reaction mixture, was carried out periodically (three times). Separation of the ester products from the un-

reacted *n*-hexadecane was achieved by chromatography of the crude mixture (25 ml) on Spence (Registered Trade Mark) Type A alumina (500 g). The *n*-hexadecane was eluted from the column using 60–80° petroleum ether. The esters were removed from the column using a 1:1 solvent mixture of toluene and 60–80° petroleum ether. The total ester yield from the reaction was 23.9 per cent

weight (based on ethyl diazoacetate). Elemental analysis, infra-red and mass spectroscopic data confirmed that the expected ester mixture $C_{11}H_{22}CO_2Et$ was present. The respective proportions of the ester isomers were determined using gas liquid chromatographic techniques and the results are tabulated below:—

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| Position of Carboethoxycarbene Insertion in <i>n</i> -Hexadecane | Ester Formed | Ester in Total Ester Product (% wt) |
|--|---|-------------------------------------|
| C_1 | Ethyl Stearate | 12.2 |
| C_3 | Ethyl 3-Methylheptadecanoate | 17.1 |
| C_5 | Ethyl 3-Ethylhexadecanoate | 13.4 |
| C_4 | Ethyl 3-Propylpentadecanoate | 12.2 |
| C_6 | Ethyl 3-Butyltetradecanoate | 11.5 |
| $C_6 — C_8$ | Ethyl 3-Pentyltridecanoate Ethyl 3-Hexyldodecanoate Ethyl 3-Heptylundecanoate | 33.6 |

20 It can be seen that branched chain esters comprised about 88 per cent weight of the ester mixture.

be repeated without isolation of the esters until, for example, a 10 per cent weight yield of esters (based on hydrocarbon) was obtained.

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EXAMPLE 2

Reaction with *n*-Hexadecane

25 A mixture of *n*-hexadecane (678 g, 3.0 mol) and ethyl diazoacetate (3.42 g, 0.03 mol) was stirred and irradiated at 35° in a 1 litre medium pressure mercury arc reactor for 16 hours. A molar ratio (hydrocarbon/carbene precursor) of 100:1 was used. The yield of monoesters was 55 per cent weight (based on ethyl diazoacetate). After removal of the thin wall-deposit from the inner surface of the reaction similar photolysis of a further quantity of ethyl diazoacetate (3.42 g, 0.03 mol) in the reaction product again gave a 55 per cent weight yield of esters and this process could

EXAMPLE 3

Reaction with *n*-Docosane

45 *n*-Docosane is a solid at room temperature so the temperature of the photolysis was increased to 50°C. A mixture of *n*-docosane (21.3 g, 0.07 mole) and ethyl diazoacetate (3.99 g, 0.035 mole) i.e. a molar ratio of 2/1, hydrocarbon/carbene precursor was irradiated at 50° in a medium pressure mercury arc reactor for twenty hours. The yield of ester product was low (5.6 per cent weight based on ethyldiazoacetate). The composition of the crude ester mixture was established using gas-liquid chromatographic techniques and is given below:—

50

| Position of Carboethoxycarbene Insertion in <i>n</i> -Docosane | Ester Formed | Ester in Total Ester Product (% wt) |
|--|--------------------------------|-------------------------------------|
| C ₁ | Ethyl <i>n</i> -Tetracosanoate | 8.9 |
| C ₂ | Ethyl 3-Methyltricosanoate | 12.0 |
| C ₃ | Ethyl 3-Ethyldocosanoate | 9.6 |
| C ₄ | Ethyl 3-Propylheneicosanoate | 9.2 |
| C ₅ | Ethyl 3-Butyleicosanoate | 9.0 |
| C ₆ — C ₁₁ | — | 51.3 |

EXAMPLE 4

Thermal Reaction with *n*-Hexadecane

- 5 A solution of ethyl diazoacetate (1 g, 0.0088 mol) in *n*-hexadecane (25 g, 0.11 mol) was added over a period of 5 hours to *n*-hexadecane (25 g, 0.11 mol) maintained at 170°C under an inert atmosphere. The total molar

ratio (hydrocarbon/carbene precursor) used was about 25:1. The mixture was heated for a further 2 hours at 170°C. The yield of esters was 82 per cent weight (based on ethyl diazoacetate) and the composition of the ester mixture as determined using gas liquid chromatographic techniques is given below.

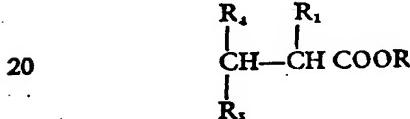
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| Position of Carboethoxycarbene Insertion in <i>n</i> -Hexadecane | Ester Formed | Ester in Total Ester Product % wt |
|--|---|-----------------------------------|
| C ₁ | Ethyl stearate | 9.9 |
| C ₂ | Ethyl 3-methylheptadecanoate | 15.7 |
| C ₃ | Ethyl 3-ethylhexadecanoate | 13.6 |
| C ₄ | Ethyl 3-propylpentadecanoate | 13.0 |
| C ₅ | Ethyl 3-butyltetradecanoate | 12.8 |
| C ₆ — C ₈ | Ethyl 3-pentyltridecanoate Ethyl 3-hexyldodecanoate Ethyl 3-heptylundecanoate | 35.0 |

WHAT WE CLAIM IS:—

1. A method of preparing esters of general formula



where R₄ and R₂ are saturated straight chain hydrocarbyl radicals which together contain at least eleven carbon atoms, R₁ is hydrogen or an alkyl radical and R is a hydrocarbyl radical, which comprises reacting a saturated

straight chain hydrocarbon having at least twelve carbon atoms with a carbohydrocarbyloxy carbene of general formula: CR₁COOR where R and R₁ are as defined above.

2. A method as claimed in claim 1 in which the hydrocarbon is a C₁₂— paraffin.

3. A method as claimed in claim 1 or 2 in which the carbene is prepared in situ by the decomposition of a carbene precursor.

4. A method as claimed in claim 3 in which the carbene precursor is a diazo compound, a ketone or a diazirine.

5. A method as claimed in claim 4 in which the diazo compound is an alkyl diazo-carboxylate.

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6. A method as claimed in any one of claims 3—5 in which the carbene precursor is decomposed by irradiation. 10
7. A method as claimed in any one of claims 3—5 in which the carbene precursor is decomposed by the action of heat. 15
8. A method as claimed in any one of claims 3—7 in which the carbene precursor is added to the hydrocarbon in a molar ratio of hydrocarbon: carbene precursor at least 2:1.
9. A method of preparing esters as claimed in claim 1 as hereinbefore described with reference to the Examples.
10. Esters when made by the method of any one of the preceding claims.

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